

Differences in FTIR spectra measured in olivines derived from depleted and metasomatised sections of the Earth's mantle

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The defect structure of olivine depends on the conditions of its crystallization/equilibration [1]. The concentration of various hydrogenated point defects in the olivine structure can be measured using FTIR spectroscopy. The position and intensity of OH IR absorption peaks reflect differences in pressure and silica activity (a_{SiO_2}).

We measured FTIR spectra of olivines from different types of mantle xenoliths: depleted diamondiferous harzburgites from the Finsch kimberlite, olivine xenocrysts from metasomatized cpx-rich mantle under the Superior Craton carried to the surface within Victor kimberlite, and an equigranular amphibole-bearing xenolith (DW211) from Dreiser Weiher (Eifel) [2].

Olivines from depleted harzburgites show different FTIR spectra compared to olivines from xenolith which likely interacted with low a_{SiO_2} melts (carbonatitic, alkaline-rich calcic melts). While olivines from both groups of samples showed IR OH absorption bands in the wavenumber range between 3440 and 3650 cm^{-1} , peaks at 3356 and 3328 cm^{-1} were observed only in olivines from non-metasomatised peridotites. Such peaks were also commonly observed in olivines experimentally equilibrated with orthopyroxene at hydrous conditions [1, 3]. The observed absence of lower frequency IR OH absorption bands could be due to deficit of the octahedral defects in the olivine defect structure, which is likely to occur at low a_{SiO_2} conditions [1]. In spite of a hydrous character of kimberlitic magmas some of the xenocrystic olivine macrocrysts from the Victor kimberlite did not contain hydroxyl in spectroscopically detectable quantities. This observation is consistent with results of hydration experiments performed on olivines from DW211 where olivine cores with diameters <1 mm remained anhydrous after 4 hours runs, conducted at 2 GPa and 1000°C. This could be due to an adjustment of the defect structure to changing a_{SiO_2} conditions.

The results of this study suggest that FTIR spectroscopy of mantle olivine can be used as a complimentary tool to detect cryptic low a_{SiO_2} metasomatic events.

[1] Matveev *et al.* (2001) *J. Petrol.* **42**, 721-729. [2] Witt-Eickschen *et al.* (2003) *J. Petrol.* **44**, 1077-1095. [3] Berry *et al.* (2005) *Geology* **33**, 869-872.

Impact of organic co-contaminant complexation on Th sorption to sand

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Understanding radionuclide speciation is fundamental to predicting the behaviour of radioactive contaminants in the environment. Specifically, the distribution of radionuclides between solid and solution phases will be determined by a combination of physico-chemical parameters, particularly pH and ligand availability, that control speciation. Anthropogenic chelating agents such as ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid are common complexing agents that are present as co-contaminant species in low and intermediate level nuclear wastes. They form stable complexes with tri- and tetra-valent cations, and it is known that complexation will increase radionuclide solubility and hence mobility; they are therefore of particular interest when assessing environmental risk from radioactive contaminants. This presentation will detail our work investigating aqueous radionuclide-ligand speciation, and the effect of speciation on radionuclide sorption using thorium as model tetravalent actinide.

Electrospray ionisation mass spectrometry (ESI-MS) was used to provide direct observation of aqueous Th complexation with EDTA and NTA, and the impact of these species on Th sorption was assessed in a series of batch experiments using a relevant environmental sand matrix and 1:1 molar ratios of Th:ligand. Thorium and Th-complexes showed slow sorption kinetics, and reached equilibrium partitioning by 7 d. At pH 4, [ThEDTA] and [ThNTA]⁺ species dominate in aqueous solution, and the sorption behaviour of these species was concentration dependent. At 5 μM concentration, the ligands enhanced the interaction of Th with the solid phase, but at 400 μM concentration, the ligands increased its solubility. At pH 8, the dominant EDTA species included [ThEDTA(OH)]⁻, and the only NTA species detected was [Th(NTA)₂]²⁻. These species were significantly more soluble than Th at both 5 and 400 μM concentrations, which is consistent with their anionic forms. Determination of the dissolved organic carbon quantified ligand interactions with the solid phase, thus the overall sorption mechanisms will be described and presented within a geochemical model.